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RATE OF METHANE OXIDATION CONTROLLED BY FREE RADICALS

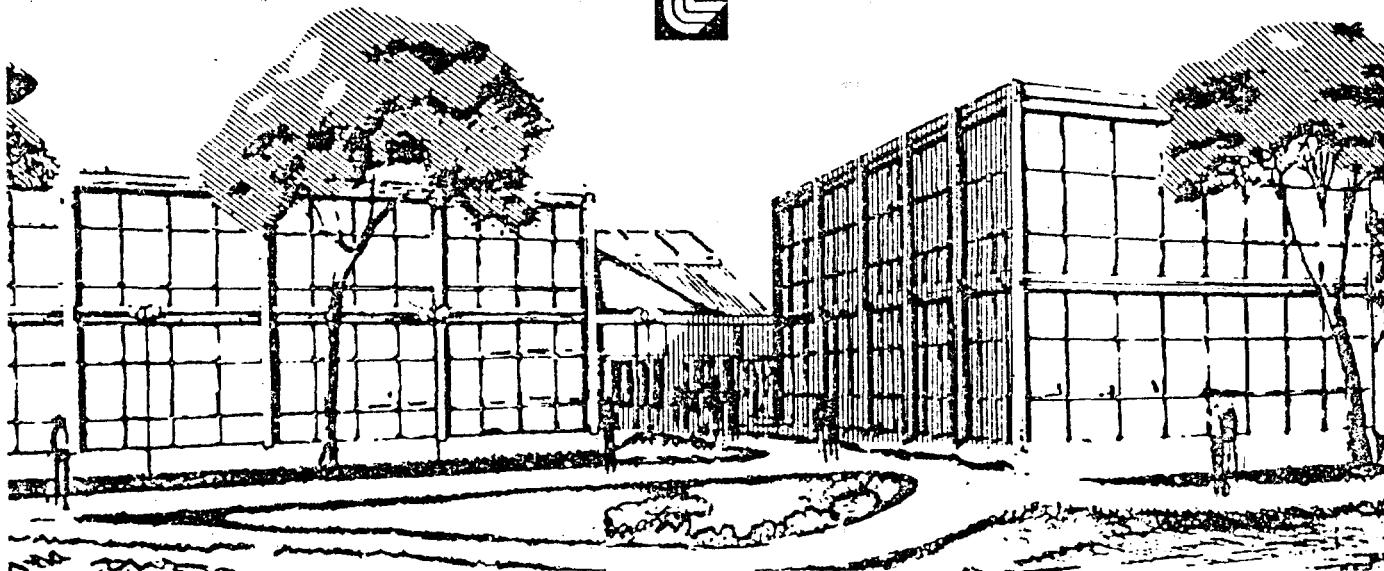
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RATE OF METHANE OXIDATION CONTROLLED BY FREE RADICALS.

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A simple model of the chemical processes governing the rate of heat release during methane oxidation will be presented below. There are simple models for the induction period of methane oxidation (1,2,3); and the partial equilibrium hypothesis (4) is applicable as the reaction approaches thermodynamic equilibrium. However, there are apparently no previous successful models for the portion of the reaction where fuel is consumed rapidly and heat is released. There are empirical rate constants which, due to experimental limitations, are generally determined in a range of pressures or concentrations which are far removed from those of practical combustion devices. To calculate a practical device these must be recalibrated to experiments at the appropriate conditions, so they have little predictive value and give little insight into the controlling physical and chemical processes. The model presented here is based on extending Semenov's model (2) of the induction period to cover the period of heat release.

Semenov's model considers any branching chain reaction. It assumes that some initial dissociation of fuel leads to an intermediate species. This species, or some of its products, reacts with the fuel to create more of the intermediate species, implying branching reactions. If recombination, or other chain breaking reactions, are allowed one gets a rate equation for the concentration of the intermediate species $[R]$.

$$d[R]/dt = A + B[R] - C[R]^2 \quad (1)$$

The first term on the right represents the initial dissociation, the second the branching chain reactions, and the third recombination. Coefficients A, B and C are functions of the rate constants and the concentration of fuel and oxidizer, but are independent of the intermediate concentration.

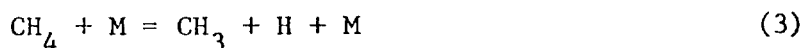
Creighton (3,5) has shown that the induction period of methane oxidation is described by Semenov's model. Analysis of the results of numerical calculations using a detailed chemical kinetics reaction scheme showed that about eight reactions were dominant, and that the rate of creation and consumption of

species H, OH and O were balanced. This justified using a steady state approximation on the corresponding rate equations yielding algebraic equations which couple the concentration of these species to one another and to $[CH_3]$. The rate limiting step was found to be



with rate constant $k_2 = 2 \times 10^{13} \exp(-14,500/T) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ (1). The CH_3O immediately decomposes to CH_2O and H. It can be shown (3,5) that branching reactions of H immediately result in three new CH_3 radicals and branching reactions of O yield two more. Thus branching reactions yield five new CH_3 for every one consumed by reaction 2, a net increase of 4. This establishes a value for Semenov's coefficient $B = 4k_2[O_2]$. (There is some controversy concerning reaction 2 and the value of k_2 , but it gives calculated induction times in agreement with a wide variety of experiments (3). The reaction may proceed via an intermediate complex, CH_3O_2 ; but this gives the same calculated induction time provided it decomposes in steps which give H and O atoms rather than OH, and that decomposition is faster than reaction 2.)

Coefficient A depends on the initial dissociation step,



with rate constant $k_3 = 2 \times 10^{17} \exp(-44,200/T) \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ (9). Branching reactions of the H atom give three more CH_3 molecules so $A = 4 k_4 [CH_4][M]$.

The rate of all recombination reactions will be proportional to $[CH_3]^2$, because all radical concentrations are proportional to $[CH_3]$. If we take the reverse of reaction 3 as a prototype, C equals $k_{-3}[M]([H]/[CH_3])$, where the ratio $[H]/[CH_3]$ is determined by the algebraic relations mentioned above and is a function only of the rate constants and the concentration of fuel and oxidizer. The magnitude of this ratio is about 10^{-3} . A value of $C = 1.7 \times 10^{14}[M]$ has been found to give calculated induction times in agreement with experiment at pressures above atmospheric, and is unimportant at low pressures.

A rate equation for fuel consumption can also be written (3,5).

$$d[CH_4]/dt = -A - 5/4 B[R] + C[R]^2 \quad (4)$$

The numerical factor 5/4 results from consumption of five molecules of CH_4 for a net increase of four CH_3 . (There should also be a small numerical correction to the last term because an H atom, as well as a CH_3 , is consumed.)

Eqs. 1 and 4 constitute a model for the induction period of methane oxidation, and can be integrated in closed form provided the temperature is held constant. If they are integrated numerically, along with appropriate thermochemistry to account for the temperature change, the solutions are a semi-quantitatively correct description of the fuel consumption, as well as induction.

Fig. 1 shows the results of such a calculation. (The model gives a rate of fuel consumption which can be as much as an order of magnitude too small. This occurs because the model neglects additional reactions which increase the ratio of $[OH]$ to $[CH_3]$ during fuel consumption.) Initially $[R]$ is zero and A is the dominant term in eq. 1, but $B[R]$ rapidly becomes larger and $[R]$ increases exponentially as seen at the left of Fig. 1. Eventually as $[R]$ increases, $C[R]^2$ becomes comparable to $B[R]$ and the time derivative becomes very small, as in the middle of Fig. 1.

The time derivative becomes small because $[R]$ approaches a quasi-equilibrium value $[R]_e = B/C$. This might also be called the steady state or stationary state, but all terminology seems to lead to possible confusion. There are two important properties of $[R]_e$. First, it is a stable solution of eq. 1 so $[R]$ will tend to stay near $[R]_e$. Second, it depends only on the rate constants and the concentration of fuel, oxidizer and diluent, but not on the radical concentration. It does have a strong temperature dependence due to the large activation energy of B . A upper limit to $[R]_e$ is shown as a dashed line in Fig. 2. This was calculated holding $[O_2]$ and $[M]$ constant at their initial values of 5×10^{-5} and 2×10^{-4} moles/cc. The actual value of $[R]_e$ will be lower than this due to consumption of fuel and oxygen.

To compare reactions with different time constants it is useful to plot them as trajectories in a multi-dimensional phase space whose coordinates are the species concentrations and the temperature. Fig. 2 shows trajectories projected onto the temperature vs. $[R]$ plane for reactions with identical initial fuel and air concentrations but different initial radical concentrations and temperature. Trajectories beginning at the left had no initial radicals, and the trajectory starting at 1200 K is represented in Fig. 1. The exponential increase of $[R]$ to $[R]_e$ is isothermal so it appears horizontal in Fig. 2. The knee of the curve represents the relatively flat portion of Fig. 1 where $[R]$ is approximately $[R]_e$. As the temperature increases $[R]$ remains approximately equal to $[R]_e$, which lies to the left of the dashed line due to consumption of fuel and oxygen. Trajectories beginning on the right had an initial radical concentration equal to half the initial fuel concentration. The radical concentration fell rapidly to $[R]_e$, releasing heat, and then remained at $[R]_e$. A heat loss term was included in the model with the result that trajectories which reach $[R]_e$ at temperatures below 1050 K do not go to complete combustion because the chemical heat release is less than the heat loss, and the mixture cools.

Fig. 2 shows clearly that the quasi-equilibrium radical concentration sets the rate of fuel consumption and chemical heat release. It also shows the stability. Whatever the initial value of $[R]$ it moves towards $[R]_e$ and remains there. It can only increase as $[R]_e$ increases with temperature. Thus, though the oxidation of methane is a branching chain reaction, fuel

consumption proceeds as a thermal reaction with the rate determined by $[R]_e$.

The quasi-equilibrium radical concentration does not depend on the assumptions of the Semenov model, although the model gives the simplest explanation. Numerical calculations using the full detailed kinetic reaction mechanism for methane oxidation (8) show that each radical species concentration is in quasi-equilibrium. During induction CH_3 has the largest concentration, but as other reactions become important $[H]$, $[OH]$ and $[O]$ become larger. Fig. 3 shows reaction trajectories on a temperature versus $[OH]$ plane for some detailed kinetics calculations. The solid line is a simulation of a low pressure, laminar flame (6) with circles representing experimental data (7). The dashed line is a constant volume, adiabatic reaction for the same mixture, an approximate simulation of fuel consumption in a shock tube or turbulent flow reactor. The value of $[OH]_e$ for the flame differs from the constant volume case because fuel is consumed at a lower temperature in the flame and $[OH]_e$ depends strongly on the fuel consumption. This is demonstrated by isothermal (constant volume) calculations of $[OH]_e$ shown in Fig. 3 as triangles for fuel concentrations equal to those in the flame as squares for the adiabatic case. The value of $[OH]$ in the flame is somewhat greater than $[OH]_e$ because radicals diffuse ahead of the flame.

We conclude that free radical concentrations control both the induction time and the rate of fuel consumption, and depend only on a few critical rate constants and the concentration of fuel and oxidizer. A more detailed report is being written and Ref. 8 discusses the implications for ignition. This work was performed at the Lawrence Livermore Laboratory for the U. S. Department of Energy under contract No. W-4705-Eng-48.

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Figure Captions

Figure 1 Calculated mole fractions of fuel, intermediate species and products using Semenov's model for a stoichiometric methane-air mixture initially at 1200 K and atmospheric pressure.

Figure 2 Reaction trajectories calculated with Semenov's model for a stoichiometric mixture at atmospheric pressure and various initial temperatures and radical concentration. The dashed line shows B/C calculated using constant initial fuel and oxygen concentrations but varying temperature.

Figure 3 Reaction trajectories calculated using a detailed kinetics model. Symbols are described in the text.

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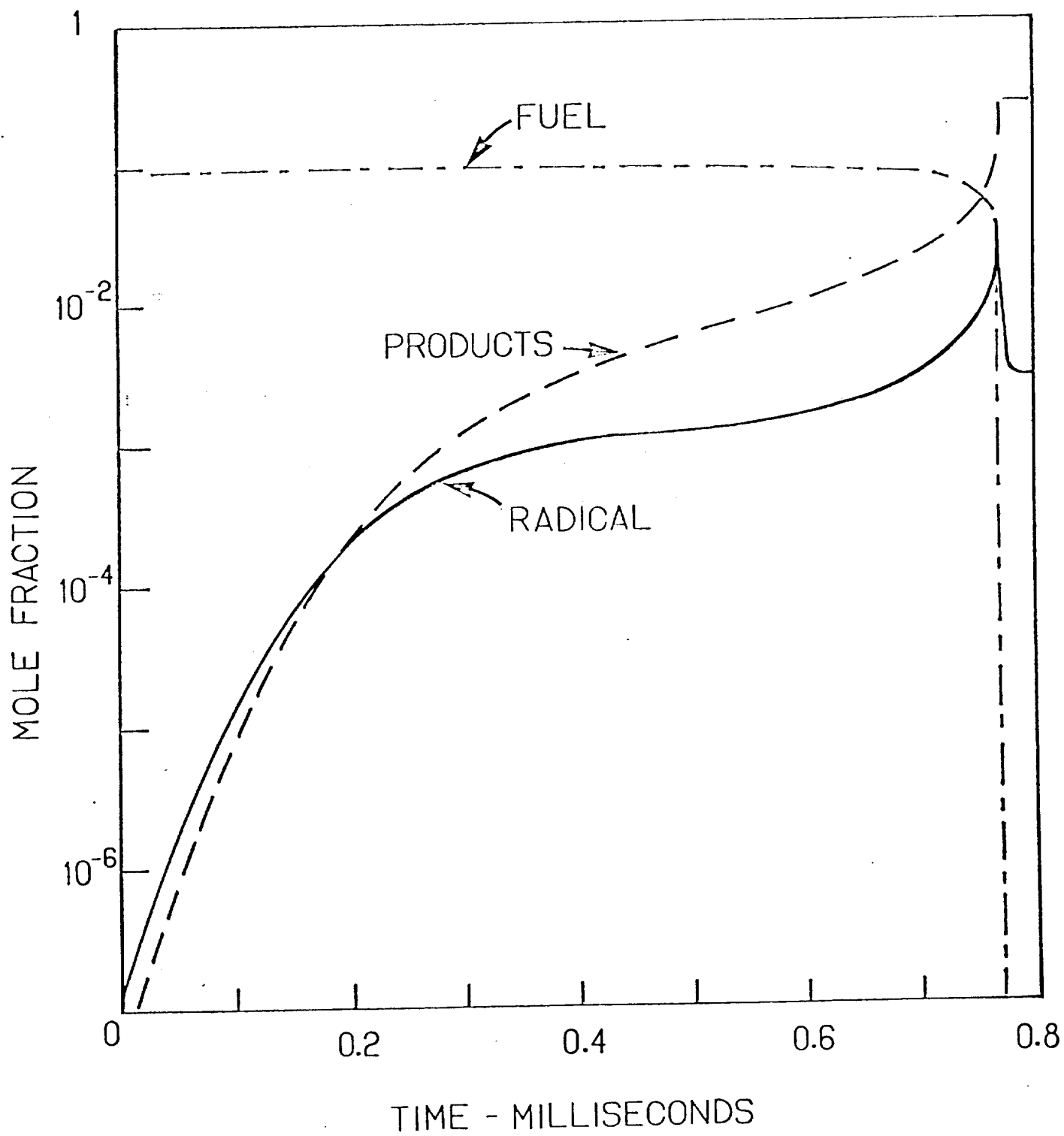


Fig. 1

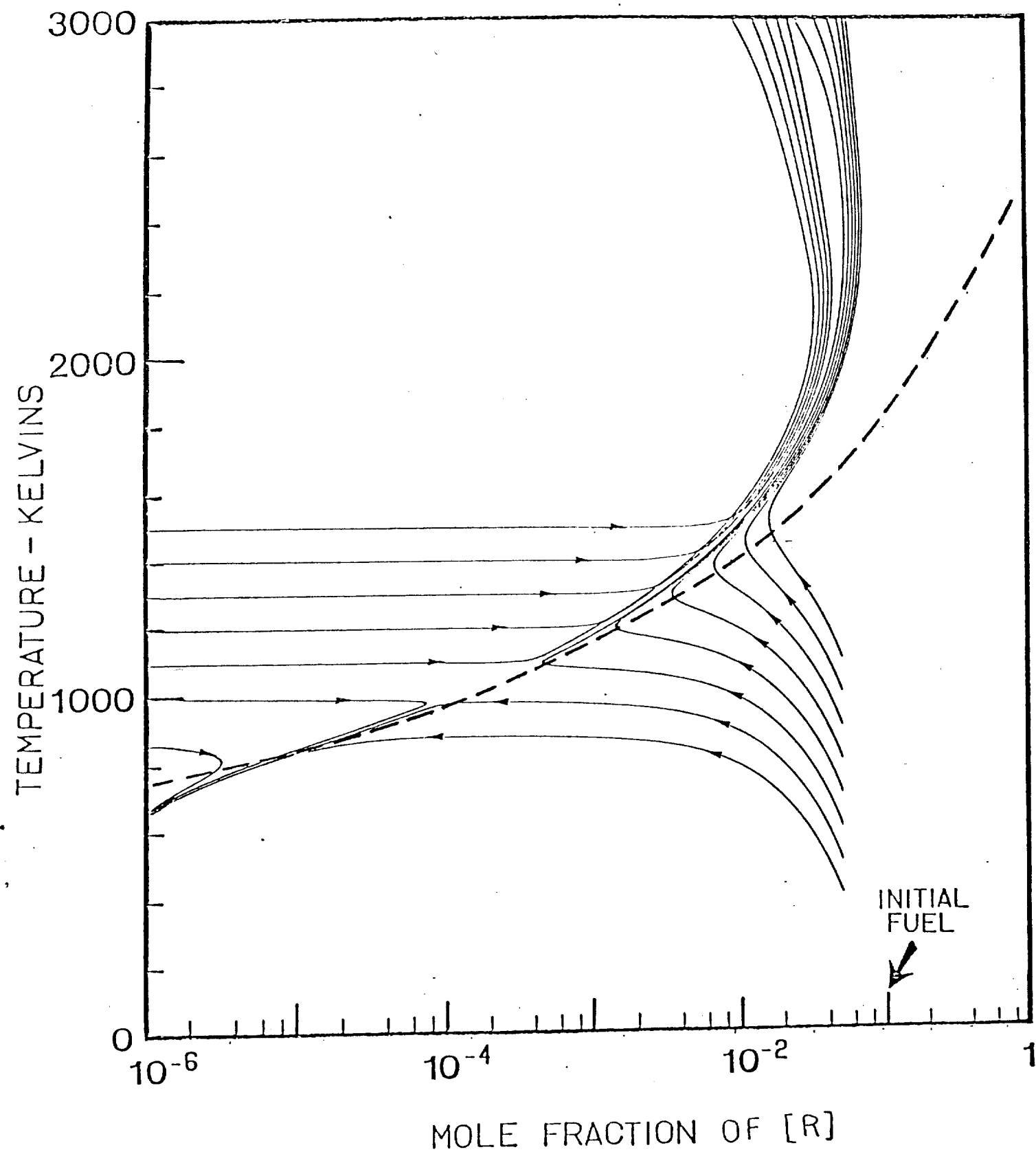


Fig 2

